PATENT ABSTRACTS OF JAPAN

(11)Publication number : 61-004232
(43)Date of publication of application : 10.01.1986

(51)Int.Cl. H01L 21/304

(21)Application number : 59-125760
(22)Date of filing : 19.06.1984

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(54) CLEANING METHOD OF SEMICONDUCTOR SUBSTRATE

(57)Abstract:
PURPOSE: To safely and readily remove any station on the surface of a silicon wafer, by dipping a semiconductor substrate in a solution of an organic acid being bubbled by ozone or oxygen and thereby treating the substrate.
CONSTITUTION: An organic acid (e.g., formic acid or acetic acid) is filled into a cleaning tank and heated (to 100W150° C). A semiconductor substrate is dipped in this liquid, and ozone or oxygen is supplied from the bottom of the tank so as to bubble the liquid, whereby the substrate is cleaned by the bubbles. Any heavy metal on the wafer forms a formate or an acetate, and any organic contaminant is decomposed by ozone, whereby stains on the surface of the substrate can readily be cleaned out.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

⑲日本国特許庁(JP)　⑪特許出願公開

⑫公開特許公報(A)　昭61-4232

⑤Int.Cl.⁴　識別記号　庁内整理番号　⑬公開　昭和61年(1986)1月10日
H 01 L 21/304　D-7131-5F

審査請求　未請求　発明の数 1　(全2頁)

⑭発明の名称　半導体基板の洗浄方法

⑪特　願　昭59-125760
⑫出　願　昭59(1984)6月19日

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明　細　書

1.発明の名称

半導体基板の洗浄方法

2.特許請求の範囲

(1)半導体基板を有機酸にオゾンノ酸素をバブルした溶液中に浸漬し、処理することを特徴とする半導体基板の洗浄方法。

3.発明の詳細な説明

〔技術分野〕

本発明は半導体基板の洗浄方法に関するものである。

〔従来技術とその問題点〕

LSI製造において、ウエハの洗浄工程は各プロセス間にゴミ、汚れを除去する数多くの処理回数を必要とし、製品の歩留り向上に重要な役割となっている。この洗浄工程で使われている主な液としてはアルカリ系と酸系に大別される。公知の洗浄液としてはアンモニア水-過酸化水素系、又は塩酸-過酸化水素系(通称RCA洗浄ともいう)。さらに、硫酸-過酸化水素系、硫酸-硝酸系等の混酸溶液が用いられている。溶液は通常60～150℃に加熱され、時には超音波を併用することもある。

しかしながら、アンモニア-過酸化水素系や塩酸-過酸化水素系では、過酸化水素がすぐにH_2Oと発生期の0に分解してしまうので、酸化力が劣化し、洗浄力が持続せず即欠的に過酸化水素を補充する必要があり、工程としては煩雑になる。硫酸-過酸化水素系も同じ理由で不利である。この硫酸-過酸化水素系や硫酸-硝酸系等は廃液として処理する場合の問題がある。それは硫酸を廃棄する場合、水と反応して100℃以上となり安全上危険があり、このため大量の水を必要とし、又硝酸を使う場合は、窒素酸化物等が発生し公害上規制される等、大量に使うことはできないという不利な点がある。すなわち、処理費用が高くなる。

又上記の酸-過酸化水素系に代る処理方法としての公知例として特公昭52-012063号の半導体基板のレジスト膜除去方法がある。この方法は硫酸を用いて過酸化水素の代りにオゾンを用いる方法

であるが、この方法では硫酸を廃液処理するのに大量の水（～10倍希釈）を必要とする等、安全上、費用の点で問題があつた。

〔発明の目的〕

本発明は安全上を図り、かつ低廉な処理を行なうことができるようにした処理方法を提供するものである。

〔発明の構成〕

本発明は有機酸を洗浄液として、槽内にオゾン／酸素をバブルしてシリコンウエハの表面汚れを除去することを特徴とする半導体基板の洗浄方法である。

〔発明の原理・作用〕

有機酸のうちギ酸は強酸で、還元性をもつている。一方、酢酸は弱酸であり、それぞれ金属(M)と反応して-COOH基のHを置換し、-COOMなる金属塩を作る。

又オゾンをバブルすることにより、有機汚染物質をオゾンにより酸化し、分解除去することができる。

すなわち、本発明は半導体基板（ウエハ）上の重金属はギ酸塩、又は酢酸塩を作り有機汚染物質はオゾンで分解することにより、洗浄を行おうとするものである。

〔実施例〕

次に本発明と従来例とを比較しながら説明する。

以下に本発明の一実施例について説明する。

本発明は洗浄槽に有機酸（例えばギ酸、酢酸）を入れ、これを加温（100～150℃）し、この液内に半導体基板を浸漬し、槽底部よりオゾン／酸素をバブルして基板において洗浄を行うものである。

本発明で用いた洗浄槽はテフロン製のものを用い、液温は投込型石英ヒーターで加熱・調節した。又オゾン／酸素は槽底部よりパイレックス製ガス分配器によりバブルして行つた。同型槽を用いて従来のRCA洗浄液の$NH_4OH-H_2O_2-H_2O$（1：1：5）で、液温～80℃、10分間洗浄を行つた。

さらに本発明による方法では、前記の同じ槽を用いて同一ロットのウエハを用いて該ウエハをギ酸又は酢酸溶液に浸漬する。このとき、この溶液を100～150℃に加温する。さらに槽底部よりオゾン／酸素をバブルして～10分間洗浄を行つた。

従来法の$NH_4OH-H_2O_2-H_2O$系溶液で洗浄したウエハと、本発明によるギ酸－オゾン－O_2系溶液で洗浄したウエハとをスチーム処理（950℃、10分H_2-O_2雰囲気）を行い、非接触法によるライフタイムを測定した結果と、MOS C-V法により評価したVFB（フラットバンド電圧）とを表－1に示す。

表－1

洗浄方法	ライフタイム(μsec)	VFB(V)
従来法（NH_4OH系）	7	-0.9
本発明の方法(オゾン/ギ酸)	20	-1.0

〔発明の効果〕

第1表に示したように本発明による洗浄方法は従来のRCA洗浄液に比べて、再結合ライフタイムの値が～3倍となり、洗浄効果が優れている事を示している。又MOS C-V法より求めたVFB（フラットバンド電圧）は従来法のものと大きな違いはなく、-1.0Vであつた。

以上のように本発明の洗浄方法は従来法との洗浄効果と比較して同等以上であり、充分に目的が達成される。

又本発明は硫酸、硝酸等が水と反応して発熱する問題が生じたり、公害上問題になることは少い。それはギ酸、酢酸は高温（～150℃）でCO, CO_2, H_2O等に分解し易いこと、オゾンによりさらに分解を促進されるためである。このため、本発明によれば、廃液するときには水にも容易に溶け、問題はなく、工業上安全、且つ合理的に作業をすることができるばかりでなく、処理に要する費用を節減することができる効果を有するものである。

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(19) **Japanese Patent Office** (JP)
(12) **Official Gazette for Unexamined Patent Applications** (A)

(11) Japanese Patent Application Kokai Publication No. S61-004232
(43) Publication Date: January 10, 1986
Number of Claimed Inventions: 1 (total of 2 pages)
Request for Examination: Not requested

(51) International Class.[4] Identification No. JPO File No.
H 01 L 21/304 D-7131-5F

(54) Name of Invention: Cleaning Method for Semiconductor Substrate
(21) Application No.: S59-125760
(22) Application Date: June 19, 1984

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Specifications

1. Name of Invention

Cleaning Method for Semiconductor Substrate

2. Claims

(1) A cleaning method for a semiconductor substrate is characterized by a process in which a semiconductor substrate is dipped into an organic acid that is fed with bubbles containing ozone/oxygen.

3. Detailed Description of the Invention

<Technical Field>

This invention pertains to a cleaning method for a semiconductor substrate.

<Prior Art & Related Problems>

During LSI production, wafers must be cleaned several times between processes in order to remove dust and dirt, and a technique for doing so has become important from the standpoint of improving production yields. The primary solutions used in such a cleaning process are generally classified into alkali and acid type solutions. Examples of well-known cleaning solutions include aqueous ammonia – hydrogen peroxide and hydrochloric acid – hydrogen peroxide (also commonly referred to as RCA cleaning) types. In addition, mixed acid solutions are used such as sulfuric acid – hydrogen peroxide and sulfuric acid – nitric acid types. Solutions are normally heated to a temperature of 60 – 150°C and sometimes undergo ultrasonic wave treatment during heating.

However, in the cases of ammonia – hydrogen peroxide and hydrochloric acid – hydrogen peroxide types, since the hydrogen peroxide quickly breaks down into H_2O and nascent-state O, the deterioration in oxide strength causes inconsistent cleaning strength. Therefore, it becomes necessary to periodically replenish the solution with hydrogen peroxide, resulting in a complicated process. Sulfuric acid – hydrogen peroxide type solutions are also unfavorable for the same reason. Problems exist in cases where these sulfuric acid – hydrogen peroxide and sulfuric acid – nitric acid types are used as waste solutions during treatment. In cases where sulfuric acid is discarded, there is a safety concern when it reacts with water and reaches a temperature of 100°C or more. For this reason, a large volume of water is needed. Furthermore, when sulfuric acid is used, nitrogen oxides are generated which need to be regulated due to pollution standards, and for this reason, sulfuric acid cannot be used in large amounts. In short, the problems noted above result in high treatment costs.

In addition, Patent No. S52-012063 describes a method for removing resist films from semiconductor substrates in a well-known treatment method that takes the place of the aforementioned acid – hydrogen peroxide type solutions. According to this method, sulfuric acid is used along with ozone, which takes the place

of hydrogen peroxide. However, according to this method, a large volume of water (up to a tenfold dilution) is required in order to discard the sulfuric acid, which presents a problem from the standpoint of safety as well as cost.

<Purpose of the Invention>

The purpose of this invention is to present a treatment method in which it is possible to maintain a high level of safety as well as a low cost.

<Constitution of the Invention>

The method for cleaning semiconductor substrates as described in this invention is characterized by a process in which an organic acid is used as a cleaning solution and bubbles containing ozone/oxygen are fed into the solution tank in order to remove dirt from the surface of silicon wafers.

<Principle/Operation of the Invention>

Among the various types of organic acids, formic acid is a strong acid that contains reduction properties. On the other hand, acetic acid is a weak acid in which the hydrogen within the –COOH group becomes displaced once the acetic acid reacts with the various heavy metals (M), resulting in the formation of a –COOH metallic salt.

Furthermore, by feeding bubbles containing ozone into the solution tank, organic contaminants become oxidized by the ozone, making it possible to remove these contaminants through decomposition.

In other words, this invention seeks to conduct a cleaning operation in which heavy metals located on top of semiconductor substrates (wafers) create formic acid salt or acetic acid salt, and organic contaminants are decomposed through the use of ozone.

<Embodiments>

The following is an explanation of this invention in which a prior example is used for comparison.

First, an embodiment of this invention will be explained.

According to this invention, the cleaning operation is conducted as follows. A cleaning tank is filled with an organic acid (such as formic acid, acetic acid, etc.), and the solution is heated (to a temperature of 100 – 150°C), after which a semiconductor substrate is dipped into the solution. Ozone/oxygen bubbles are fed from the bottom of the tank and clean the substrate as they hit up against the surface.

The tank used in this invention is made of Teflon, and the solution temperature is controlled through the use of an immersion type quartz heater. The ozone/oxygen bubbles are fed into the tank from the bottom using a gas distributor made of Pyrex. The same type of tank is used to conduct cleaning with a prior form of RCA cleaning solution comprised of $NH_4OH - H_2O_2 - H_2O$ (1:1:5) at a solution temperature of 80°C for 10 minutes.

In addition to using the same tank described above, the method of this invention calls for the use of a wafer from the same lot, and said wafer is to be dipped into a solution of formic acid or acetic acid. While the wafer is within the tank, the solution is heated to a temperature of 100 – 150°C. In addition, ozone/oxygen bubbles are fed through the bottom of the tank so that cleaning can be conducted for a period of 10 minutes.

The wafer that is cleaned using the $NH_4OH - H_2O_2 - H_2O$ solution according to the prior method, and the wafer that is cleaned using the formic acid – ozone – O_2 solution according to this invention both undergo a steam treatment (in an environment of $H_2 - O_2$ at 950°C for 10 minutes), after which lifetime measurements are conducted using a non-contact method. These results are shown in Table 1 along with the V_{FB} (Flat Band Voltage) figures, which are evaluated using the MOS C–V method.

Table 1

Cleaning Method	Lifetime (μ sec)	V_{FB} (V)
Prior Method (NH_4OH)	7	-0.9
Method of this Invention (Ozone/Formic Acid)	20	-1.0

<Effect of the Invention>

As shown in Table 1, the cleaning method described in this invention has a recombination lifetime value that is approximately three times that of the RCA cleaning solution from the prior method, which indicates a superior cleaning effect. In addition, the V_{FB} (Flat Band Voltage) figure obtained through the MOS C–V method shows a level of –1.0V, which is not significantly different from the result shown for the prior method.

Based on the above, the cleaning method described in this invention provides a cleaning effect that is equal to or greater than that of the prior method, thus sufficiently achieving the purpose stated above.

In addition, the problem noted above with respect to the generation of heat due to the reaction between water and sulfuric acid or nitric acid is prevented, thus this invention creates very few problems from the standpoint of pollution. This is due to the fact that formic acid and acetic acid can be easily decomposed into CO, CO_2, H_2O, etc., at high temperatures (up to 150°C), and this decomposition is further advanced through the use of ozone in the treatment process. As a result, this invention poses no problem with regard to discarding the solution since it can be easily dissolved in water. This not only makes it possible to provide industrial safety as well as a rational manufacturing operation, it also makes it possible to reduce the level of cost required to conduct the treatment process.

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